Dissolution, crystallisation and regeneration of cellulose in N-methylmorpholine N-oxyde

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Abstract

Mixtures of N-methylmorpholine N-oxyde (NMMO) and water are direct solvents for cellulose, used for processing fibres (Lyocell process). The objective of this work is to study three aspects of the preparation of cellulose objects from NMMO-water solutions, the NMMO-water phase diagram in order to follow the dissolution-swelling path, the crystallisation of the cellulose solution that may occur under cooling and the regeneration of the cellulose from a solution.

Introduction

N-methylmorpholine-N-oxide (NMMO) hydrates are direct solvents for cellulose, used commercially in the preparation of homogenous cellulose-NMMO-water solutions for manufacturing fibres, films and three-dimensional cellulose objects. The production of cellulose objects by the NMMO process passes through the critical step of the dissolution in the NMMO-water mixture (need of a complete phase diagram) and of the diffusion-driven precipitation of cellulose in a precipitating bath. In order to precipitate cellulose from cellulose-NMMO-water solution, the liquid coagulating agent must be miscible with NMMO and a non-solvent for cellulose. Polar liquids, like water or alcohol, are used as coagulation agents because they are miscible with NMMO and cause its removal from cellulose solution. It can be expected that the precipitation of cellulose follows the well known principles of phase separation in polymer solutions valid in such a shaping process as the membrane formation. The coagulation kinetics and the morphological features of cellulose precipitated from cellulose-NMMO-water solutions are two important aspects of this process stage. The formation of the structure depends on the mode and kinetics of precipitation of cellulose.
Finally, cellulose solution must have to be crystallised to be transported. This has also to be investigated.

Experimental

Cellulose solutions were prepared in the following manner in the Lenzing AG research centre. A small amount of gallic-acid propylester (GPE) was mixed in NMMO/water solutions and stirred during 10 min. Then, a given amount of cellulose pulp was impregnated at room temperature for one hour in a NMMO/water/GPE solution (~50 wt.-% of NMMO) using a shovel kneader equipment. After the impregnation time, the excess of water was distilled off by heating and evaporation. The pressure in the apparatus was fixed at 250 mbar and it was lowered every 5 min by 25 mbar until it reached 50 mbar. The dissolution process was ended

when the amount of distilled water was reaching the nominal value. Finally, the pressure was brought up to 400 mbar and the temperature was fixed at 108°C-112°C. The dope was maintained 15 min under these conditions.

Results and Discussion

Phase diagram

The full phase diagram of NMMO-water mixtures is given in Figure 1 [1]. It is built from DSC experiments of many NMMO-water compositions with several calorimeters in two different locations. We will describe it part by part, starting from pure NMMO. In the following, the NMMO-water mixtures will be noted nH_2O-NMMO, n being number of water molecules per NMMO molecule.

Compositions with $0<n\leq1$ (anhydrous to monohydrate)

The phase diagram is the one that has been already published. We show explicitly here the two crystallographic forms of the anhydrous part.

Compositions with $1<n\leq2.5$ (monohydrate to 2.5 hydrate)

The phase diagram in the $1<n\leq2.5$ region shows clearly the existence of a eutectic or a stable crystalline hydrate, a fact already recognised. The melting temperature of this compound is 40°C. The region above n=2 is only the beginning of a two-phase composition with what looks like a liquidus and a solidus, not related to the $1<n<2$ compositions. This rules out the fact that the crystalline entity melting at 40°C is a 2.5 hydrate, as claimed in reference. Owing

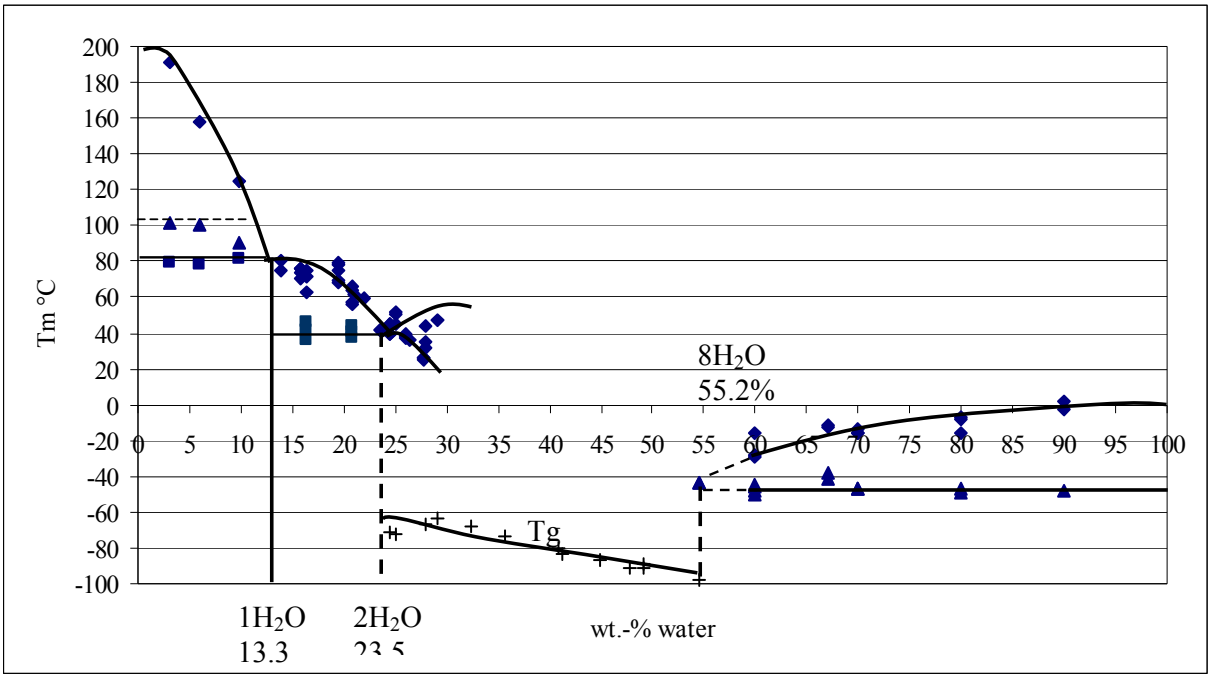

Figure 1 : Phase diagram of the NMMO-water mixtures

to the large number of independent experiments that were made, we believe that there exists a crystalline dihydrate melting at 40°C.

Compositions with 2.5<n<8

In this region, only very weak DSC events are recorded in the –60°C - –100°C temperatures range, with the variation of specific heat ΔCp as low as 1 J/(g·C). We think that these events can be related to a glass transition.

Composition with n≥8 (from $8H_2O$-NMMO to pure water)

The DSC traces of several compositions shows clearly that two peaks are present. The sharp one at low temperature has a melting temperature slightly varying from –48°C when the mixture is close to pure water to –45°C when the mixture is close to $8H_2O$-NMMO. The wide peak has a maximum temperature from 0°C (pure water) down to –30°C when it nearly vanishes. The fact that there is no visible crystallisation at composition with slightly less water than $8H_2O$-NMMO shows that the sharp peak corresponds to the melting of $8H_2O$-NMMO, with a melting temperature of –45±3°C and a melting enthalpy of 80±10J/g. The $8H_2O$-NMMO is a new stable crystalline hydrate. Up to now were only known the monohydrate and the (2.5 or 2) hydrate.

Crystallisation of cellulose-NMMO solutions [2]

The crystallisation behaviour of the 3 wt.-% cellulose solutions (15 wt.-% of water) seems to follow what is known for polymer melts and solutions. Figure 2 shows the evolution of the crystallisation velocity of solutions of various cellulose origin as a function of temperature. The crystallisation velocity is low for low temperatures because the viscosity of solutions is high. It is also low for high temperatures because the nucleation is slowed down. For the majority of solutions, the crystallisation velocity reaches a maximum around room temperature, i.e. in the temperature range 20°C – 30°C.

Cellulose of different origins may have different structural morphologies that do not always allow a proper comparison. Nevertheless, it is here possible to compare two sets of samples, the Kraft 1/1 and the Kraft 1/2, as well as the Kraft 2/1 and the Kraft 2/2, of different molecular weights. Despite their large difference in molecular weight, their growth kinetics curves are very similar, even identical within the experimental error.

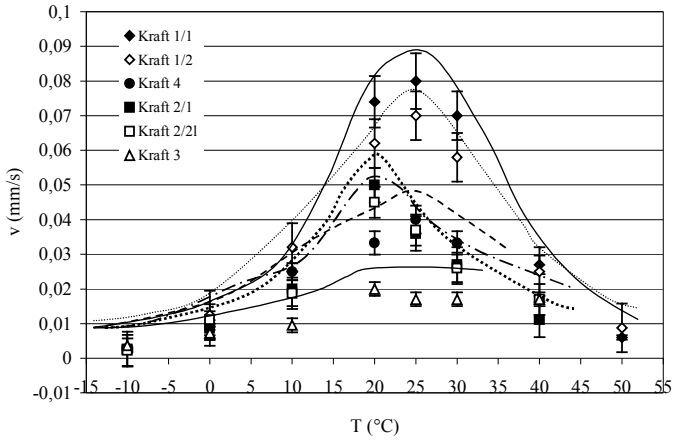

Figure 2: crystallisation velocities for different cellulose pulps

Solutions with various cellulose concentrations were investigated in order to clarify the role of the solvent during crystallisation. Plots of the crystallisation velocities of 6 wt.-%, 8 wt.-%

and 10 wt.-% Kraft 1/4 solutions are presented in figure 3. The crystallisation velocity decreases when the cellulose concentration in the solution increases. This phenomenon differs from the case of polymer solutions where the crystallisation velocity increases with concentration. This can be explained by considering that in classical polymer solutions, it is the polymer that is crystallising. So, the higher the solvent concentration is (and thus the lower the cellulose concentration is), the faster is the crystallisation. The crystallisation curves are similar to the case of the 3 wt.-% cellulose solutions, despite their maxima are not so well marked. The maximal velocity is around room temperature, as in the case of the 3 wt.-% cellulose solutions.
All observations can be explained by the fact that it is the solvent that is crystallising, not the cellulose. Another interesting conclusion is that the type of cellulose is influencing the crystallisation kinetics. We interpret this by considering the quality of the dissolution. The better the cellulose is dissolved and thus dispersed, the slower will be the crystallisation of the solvent.

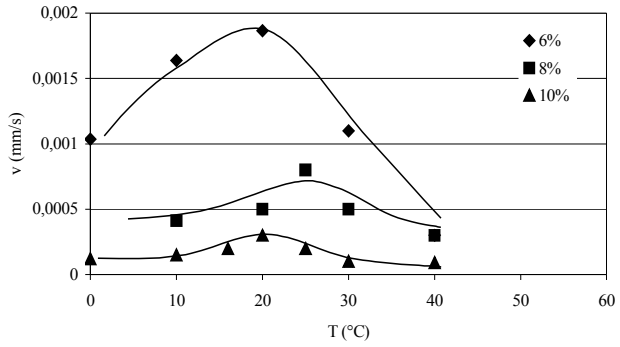

Figure 3: crystallisation velocity for different cellulose concentration

Varying cellulose concentration and origin, the crystallisation kinetics was measured as a function of temperature in the range -15°C/50°C. It is shown that the major difference with classical polymer solutions is that the crystallisation of cellulose/NMMO/water solutions is only due to the crystallisation of the solvent, not of the cellulose. The main factor controlling the crystallisation velocity is the quality of dissolution. When the cellulose dissolves well, without the formation of aggregates, the crystallisation velocity is strongly decreased.

Regeneration of cellulose from a water bath [3]

Once shaped, cellulose solutions are dropped into a non-solvent bath (water-NMMO mixtures in our case) in order to precipitate cellulose to recover a cellulose object. This was followed by measuring the diffusion coefficients at the beginning of the precipitation process of the water going from the bath to the cellulose solution and of the NMMO going from the solution to the precipitation bath. There is a large difference between these two diffusion coefficients, the first one being ten times higher than the second one. The fact that the origin and molecular weight of cellulose does not affect these diffusion coefficients implies that no major chain re-organisation occurs.

The concentration of cellulose does not affect the value of the diffusion coefficient of the non-solvent (water) from the bath into cellulose-NMMO-water solutions, which keeps a constant value of $8\ 10^{-10}$ m²/s.

The values of the coefficients of diffusion of the solvent calculated from the slopes of the diffusion curves are: 1.1 10^{-10} m²/s in the case of the solution with 6wt% of cellulose, 9.8 10^{-11} m²/s for the solution with 8wt% of cellulose and 8.1 10^{-11} m²/s for the solution with 10wt% of cellulose. Considering the data about 3wt% cellulose solutions and the data deduced from the experiments performed with 12wt% cellulose solutions (the average value is 5 10^{-11} m²/s), it is possible to plot the curve representing the evolution of the diffusion of the solvent (NMMO) from cellulose-NMMO-water solutions into the water bath versus cellulose concentration in initial solutions (Figure 4).

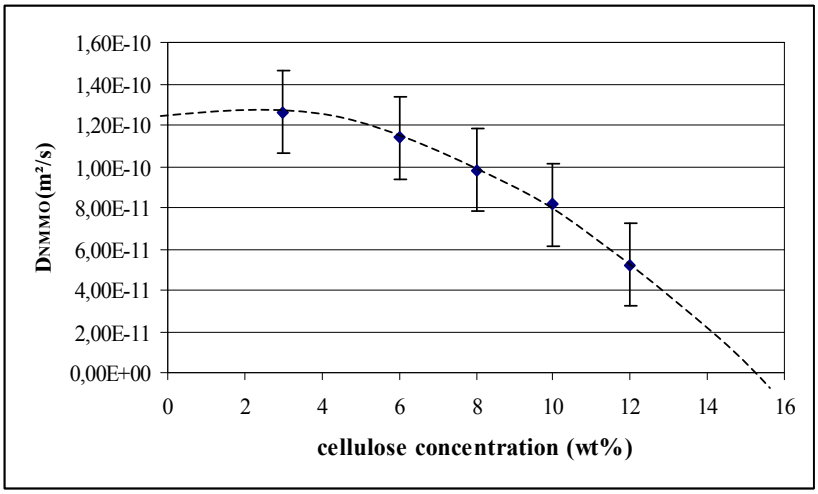

Figure 4: diffusion coefficient of NMMO leaving the cellulose-NMMO solution when placed in a water bath as a function of cellulose concentration

The fact that the diffusion coefficient of NMMO is strongly dependent on the amount of cellulose shows that despite only NMMO-water is crystallised in the solution, NMMO is strongly bound to the cellulose chain and that this controls the removal of NMMO. Figure 4 shows that the more cellulose is in the solution, the more influence it has on the diffusion coefficient. There is a mixture of free-NMMO and bound-NMMO molecules and the diffusion coefficient reflects this balance. In the low concentration region, the solution is not a mixture with cellulose everywhere. A lot of small crystals are probably interconnected. Water can diffuse quickly through these paths and the diffusion coefficient is close to the one of pure NMMO-water. This gives the plateau seen at low concentrations. From figure 4, it is possible to extrapolate the value of the diffusion coefficient of water in pure crystalline NMMO, i.e. around 1.3 10^{-9} ÷ 1.4 10^{-9} m²/s. When all the NMMO molecules are bound to cellulose, the maximal solubility is reached and the diffusion coefficient tends to very low values. Extrapolating the curve in figure 4 gives a maximal concentration of cellulose of about 14wt% to 16wt%. This maximal concentration is suggesting that above about 16wt% of cellulose, undissolved cellulose is present.

Conclusion

The phase diagram of the N-methylmorpholine-N-oxide - H_2O mixtures from 0% to 100% has been determined. Three crystalline hydrates have been identified, the already known monohydrate, a di-hydrate and a hydrate composed of 8 water molecules per NMMO. The

melting temperature of the $8H_2O$-NMMO hydrate is –47°C with a melting enthalpy of about 80J/g. When cellulose is dissolved in the NMMO-water monohydrate, the phase diagram is modified and crystallisation occurs at a much lower temperature than the pure hydrate.
When cooling down a cellulose-NMMO-water solution, only the NMMO-water is crystallising.
The regeneration of a solid, crystallised cellulose solution in a N-methylmorpholine-N-oxide – water mixture was studied by measuring the diffusion coefficient of both the water uptake from the regenerating bath and the NMMO outflow to this bath. The diffusion coefficient of water going to the cellulose solution is about 10 times larger than the diffusion coefficient of NMMO leaving the solution. This difference expresses the strongly hygroscopic character of NMMO. None of these coefficients depends on cellulose molecular weight showing that no major rearrangement of cellulose chains occurs at the beginning of the regeneration. The diffusion coefficient of water is not influenced by the cellulose concentration while the diffusion coefficient of NMMO decreases strongly when the cellulose concentration increases. Extrapolating the diffusion coefficient of NMMO versus cellulose concentration to zero shows that the maximal concentration of cellulose in NMMO-water is about 16%. Above this value, undissolved cellulose should be present.

References

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